Anomalous behavior of confined-supercooled water near the bulk water hypothetical 2nd Critical Temperature
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ABSTRACT

High resolution inelastic neutron scattering measurements of the molecular dynamics of deeply supercooled water confined to a porous host, MCM-41 are reported. Results obtained near the critical temperature of water are discussed. Anomalous behavior near and below the glass transition temperature is also presented and discussed. Results are compared to those from earlier studies on supercooled water.

INTRODUCTION

When water is confined to small spaces it exhibits significant resemblance to supercooled water. Deep supercooling can be obtained by further cooling confined water. Appropriate confinement conditions can possibly render the critical temperature of water accessible. The effects of confinement on the molecular properties of water have attracted a lot of interest in the past few decades [1-12, 14, 15, 26]. Understanding the behavior of this fascinating hydrogen bonded fluid upon confinement is of value to a vast array of problems ranging from oil recovery and geo-chemical applications to biophysical interactions, medical imaging, colloid and interface chemistry, and food product quality.

In this paper we present results of a series of inelastic incoherent neutron scattering measurements of water in MCM-41. Previous measurements on water in MCM-41 suggested dynamics on time scales of picoseconds. Here we extend these measurements using very high resolution neutron spectroscopy and find that the confined water exhibits dynamics three orders of magnitude slower than the previous measurements. Experimental detail, full instrument description and data analysis, presented briefly here are available in full detail elsewhere [24]. In this summary we focus on the interconnection between freezing point depression, glass transition temperature shift, confinement, supercooling and relaxation time distributions in water. In this experiment we have used MCM-41 samples synthesized at the University of Waterloo using a liquid crystal template. The final molar composition of the material forming the liquid crystal was: 1.0 SiO_2, 0.19 TMAOH (tetramethyl-ammonium hydroxide pentahydrate, 97%, Sigma) 0.27 CTABR (Cetyltrimethyl ammonium bromide, 99%, Aldrich), 40 H_2O. The final product was filtered, calcined and the pores saturated with H_2O. The MCM-41 pore size distribution showed a very narrow range of pores centered around 27.5 Å for an average pore diameter. The X-ray diffraction pattern from the material confirmed a hexagonal distribution of the MCM-41 channels[24].

NEUTRON SCATTERING MEASUREMENT DETAILS

Neutron scattering measurements were carried out at the NIST Center for Neutron Research on the High Flux Backscattering spectrometer (HFBS) [13].   The energy resolution of the instrument was obtained by scattering from the sample + sample holder at a temperature of 113 K. The data was collected for 5 temperatures between 213 K and 300 K, and 16 wavevector transfer (or Q) values ranging from 0.25 to 1.75 Å^{-1}. The resolution of the instrument, 0.80 µev (FWHM), was obtained by fitting a single Gaussian function to the elastic scattering at 113 K.

BACKGROUND

Inelastic neutron scattering data from water are typically analyzed using models that take into account contributions from the vibrational modes in water combined with rotational and translational diffusion contributions. The resulting structure factor is a convolution of the three structure factors corresponding to each type of motion. The motion of water molecules in the bulk at room temperature can be described as a normal stationary Markoffian random process. The position and orientation of an individual water molecule depends only on the time and distance separating it from its previous position. The motion does not carry information about initial conditions. The correlation function of water molecular motion in this case falls off exponentially with time. The exponential model has been typically adopted for analyzing relaxation data for water in confinement.

The mode coupling theory (MCT) of liquids has been widely used recently in developing models to study the behavior of glass forming liquids [14] and supercooled water [15]. It relies on the transient cage effect defined as the trapping of water/liquid molecules in cages upon supercooling of the fluid. One of its predictions is the existence of a critical temperature T_c identified as the singularity temperature for water, $T_s \sim 228$ K . Upon approaching that temperature from above the cage relaxation time becomes longer and longer until it reaches infinity at T_s, at which point the liquid reaches a state of structural arrest. This prediction is in striking agreement with the predictions from MD simulations of the SPC/E water model [15]. The MD simulations also predict a critical/singularity temperature at which water undergoes a structural arrest and where the diffusion constant becomes zero. This occurs at ~ 49 degrees below the temperature of maximum density for the SPC/E model. It also signifies the onset of vitrification as a result of a kinetic glass transition [9]. The main evidence supporting the existence of the singularity temperature comes from the power law dependence of several water relaxation parameters on temperature [16]. Since the singularity temperature is experimentally inaccessible in bulk water, it becomes necessary to look at water under confinement conditions that will allow sufficient supercooling. Chen et. al. provide a detailed derivation for the single particle intermediate scattering function (ISF) as a result of applying the mode coupling theory to supercooled water [15].

Zanotti et. al. have recently applied the predictions of MCT to supercooled water confined in porous glass. An appropriate ISF would then be obtained by multiplying the appropriate expression for a particle confined to a cage [5], with a stretched exponential factor to capture both the long and short time evolution of the relaxation.

After making some relevant approximations the final ISF has the following form [5,15].

$$I_s(Q,t) = A(Q)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{1}$$

In equation (1) $A(Q)$ is the EISF (elastic ISF)obtained for water molecules confined either to a sphere or to a hydrogen bonded cage, depending on the model used . In this paper however we do not rely on any preexisting model to obtain the EISF, and a very different explanation of the origin of the EISF used in our model is given below. An alternative approach to the study of supercooled water comes from the percolation or transient gel model [17,18,19,20] and the lattice fluid [25] model, which do not include a singularity temperature. A necessary outcome of the percolation model is a continuous distribution of correlation/relaxation times in supercooled water. A continuous distribution of relaxation times is observed in glasses and glass forming liquids.

Confinement of water results in a molecular structure and dynamics similar to those observed in supercooled bulk water [15]. Hence under proper confinement and reduced temperature conditions one should be able to access the region below the kinetic glass transition temperature. As a matter of fact, water molecules on the surface of proteins are known to exhibit glass like behavior [21].

Under these conditions, the water dynamics can be characterized by a distribution of correlation times g $(\ln\tau)$ [22], as for other glasses. The relaxation process is well represented by the Kohlrauch-Williams-Watts model, and an appropriate single particle ISF can be written as

$$I_s(Q,t) = A^*(Q)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{2}$$

There are two factors contributing to the modified elastic structure factor $A^*(Q)$ in equation (2). NMR evidence reveals water molecule dynamics in the same sample [23] and in similar samples [3] in the microsecond range, which would give an elastic contribution to the structure factor. Another contribution comes from the protons of the surface hydroxyl groups of the pore walls, which are also expected to have very slow dynamics relative to the observed timescale.

RESULTS AND DISCUSSION

The inelastic spectra were fitted to a scattering function consisting of the sum of a delta function and the Fourier transform of a stretched exponential decay convoluted with the resolution function of the instrument,

$$S(Q,E) = \left[\delta(E) + A^*(Q)FT(Se)\right] \otimes R(Q,E), \tag{3}$$

which is the Fourier transform of the following function in the time domain

$$\Phi(Q,t) = \left[R(Q)\exp\left(-\frac{t}{\tau_0}\right)^2 + A^*(Q)\exp\left(-\frac{t}{\tau_0}\right)^2 \exp\left(-\frac{t}{\tau}\right)^{\beta}\right]\exp(i\varphi(Q)t). \tag{4}$$

The first term in the bracket is an amplitude multiplying the Fourier transform of the resolution function of the instrument, best represented by a single Gaussian decay. The value of τ_0 was determined at each Q value from the 113 K data. The second term in the

bracket is the ISF for water. The last term in the equation is a complex phase factor to take care of the zero frequency offset in the spectrum. The Fourier transform was carried out numerically such that each data point in the frequency domain was assigned a corresponding point in the time domain.

A sample spectrum is shown in figure 1. The points represent the data at Q=1.1 Å^{-1} and the solid line is the fit using the model given in equation 4.   The dependence of the relaxation rate $(1/\tau)$ on Q for the various temperatures is presented in figure 2. The relaxation rate increases with increasing Q, and the best fit to the data reveals a power law dependence of the relaxation rate on Q in keeping with previous results obtained for water confined in vycor [5]. There is some deviation from the DQ^2 scattering law as the power takes on values between 1.2 and 2.4, (Table 1) increasing as the temperature increases.
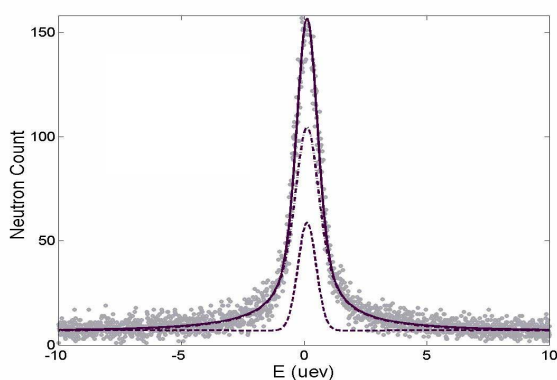

FIGURE. 1.   High Resolution inelastic Neutron scattering data taken at 223 K at a Q of 1.1 Å^{-1}. The circles are the neutron counts, and the solid line is the best fit to the data. The solid line is a convolution of the resolution function with a stretched exponential function which are also shown individually. The convolution was carried out according to equation 4.

Legend: • Data ———   Fit
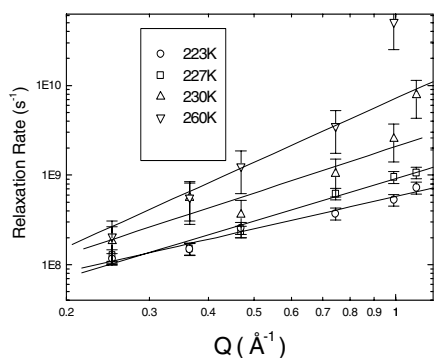   ---·---- KWW   ------- Resolution

FIGURE. 2.   The relaxation rate $(1/\tau)$ for water as a function of Q. The log-log plot shows evidence of a power law dependence. The Q range shown is 0.25-1.2 A^{-1}.

Previously reported values for the power γ are typically larger than 2 [5, 22], for our data this is also true for the highest temperature. The data taken at 223 K, 227 K and 230 K gives values for γ that are less than 2. This is an interesting result, and further investigation is warranted to find the physical reasoning behind such behavior. It should be noted that most measurements on supercooled water rarely venture near the critical temperature of ~228 K, and the three anomalous temperatures in this case are either very close to or below that value.

One might also be inclined to conclude that such a behavior could be attributed to the fact that the theoretical freezing temperature of the pores is being approached, as predicted by the Kelvin equation. Although water molecules are in the glassy phase, a significant portion is expected to be frozen [12,22], this is a very interesting region where water is most likely making the smooth transition from the liquid to the frozen state. In order to delineate the two effects it would be desirable to observe water near the freezing temperature in a larger pore size and near the critical temperature in a smaller pore size.

The data also shows a sharp increase in slope in the log-log plot of the relaxation rate vs. Q at around Q=1.2 $\AA^{-1}$. No quantitative conclusions can be made due to the very poor signal to noise ratio in that Q range. It does however seem to indicate a further divergence at higher Q values from the hydrodynamic behavior of water, which one should be able to recover at sufficiently low Q values in the case of the 260K data, and within experimental error, the 230K data.

CONCLUSIONS

The mode coupling theory has been very successful in describing single water molecule dynamics in the weakly supercooled state. However, due to the small confining radius of the pores used in this study a more appropriate theoretical framework would take into account the glass like behavior of the confined water. No free water is expected to exist within such a small pores . The behavior of the water molecules no longer reflects the weak supercooled region. Confining water molecules to small pores causes supercooled like behavior in water. Further supercooling of water is allowed because of the size of the pores, which indicates the water inside the pores of MCM-41 within the temperature range used in this experiment are deeply supercooled. An elastic scan over temperature showed no phase transition in water over the 113K-300K (Data not shown) showed no evidence of a phase transition of water in the pores, or the expected glass transition near 130K. The only transition observed, overlapped with the freezing temperature range of the water in the pores. This indicates the possibility that the glass transition temperature had shifted upward significantly due to confinement in such small pores and that it is not too far from the freezing temperature water in the pores. This is the subject of a presently ongoing investigation.

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